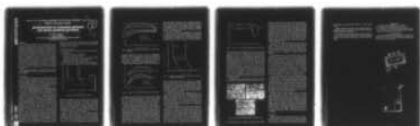AD-A037 699　　ARMY ELECTRONICS TECHNOLOGY AND DEVICES LAB　FORT MON--ETC　F/G 10/3
　　　　　　　　　BATTERY CHARGING SESSION. INVESTIGATION OF CHARGING METHODS FOR--ETC(U)
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MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

Battery Charging Session

INVESTIGATION OF CHARGING METHODS FOR NICKEL-CADMIUM BATTERIES

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Introduction

For many years alternating current superimposed on direct current and periodic reverse current have been employed by the electroplating industry for the purpose of attaining smooth and bright electrodeposits. Several reports have been made on the effects of charging batteries by pulsing or periodic reverse current. Romanov[1] reported several effects on silver-zinc batteries by means of asymmetric a.c. charging, namely; (a) the capacity was significantly increased, and (b) the argentic activity on subsequent discharge was greatly suppressed. Wales[2] reported that the capacity of sintered silver electrodes in KOH solutions increased by 40 percent when the charge was made by a 60 Hz asymmetric a.c. current at the 20 hour rate at 25°C. For lead-acid batteries, Vijayavalli et.al.[3] reported that superimposed a.c. improved the rate of lead dioxide formation.

This paper presents data on the effects of pulse and direct current charging on the electrical performance of nickel-cadmium batteries.

Experimental

A Gould Rapid Charger, designed and constructed for the US Army Electronics Command, was used for this study.[4] The charger, having the capability of operating in a d.c. mode or in several different pulse modes, has the necessary controls for varying the pulse charge current, pulse discharge current, charge interval, discharge interval, and frequency.

The vented nickel-cadmium battery employed in the parameter study of charging methods was a five cell BB-616 Battery of 5.5 Ah rating, manufactured by Eagle-Picher (E.P.).

Charging at the various test modes was carried out at rates between C/2 and 4C and in a temperature range of −40°F to 125°F. For these tests a Tenney Environmental Chamber was employed. The batteries were equilibrated at the specified temperature on an overnight stand prior to charging. No topping charges at low rates were employed in this investigation. The input was 100 percent of the theoretical capacity of the cadmium anodes, which was 12.0 Ah. The theoretical capacity of the nickel cathodes was 7.3 Ah. All discharges were carried out at the C rate at room temperature ambient to 1.0 volt per cell to determine the capacities of the nickel cathodes. To determine the capacity of the cadmium anode, a partially charged nickel hydroxide reference electrode was used and the discharging was carried in reverse until the half cell potential of the cadmium anode dropped to 0.2 V. All potentials were recorded on a Hewlett-Packard 7100 B strip chart recorder. Oscillographic traces of the charging characteristics of the batteries were measured by means of a

Tektronix 564 Oscilloscope. Micrographs of the cadmium anodes were taken using an Advanced Metals Research 900 scanning electron microscope.

Discussion and Results

Employing the Gould Rapid Charger, four charging modes were investigated:

   a. Constant current d.c. (the control)
   b. Positive pulse charge at 60 Hz
   c. Romanov[1]—type reflex charge at 60 Hz—the reflex charge consists of positive and negative pulses.
   d. McCulloch—type reflex charge at 60 Hz

Wave forms of the pulse charging modes are shown in Figure 1 as current in amperes versus time in milliseconds.
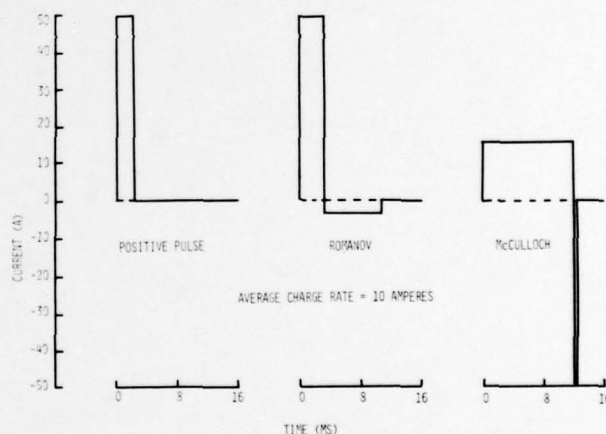

Figure 1. Pulse Charge Mode Wave Forms.

The average charge rate was 10 amperes, or the 2C rate. Square wave pulses were employed throughout the parameter study on charging methods. The wave forms of the three pulse modes are quite different; the positive pulse charge mode has no discharge pulse, the Romanov mode has a discharge pulse of 3 amperes for an 11 millisecond interval, and the McCulloch mode has a discharge pulse of 50 amperes for an interval of approximately 0.2 milliseconds.

Figure 2 shows the capacity of the nickel hydroxide (NiOOH) cathodes and cadmium (Cd) anodes as percent of theoretical capacity versus charge temperature for the four charge modes. The average charge rate was 2C. The data show that: (a) the capacity of the nickel and cadmium electrodes was about 10 to 15 percent greater with the Romanov and
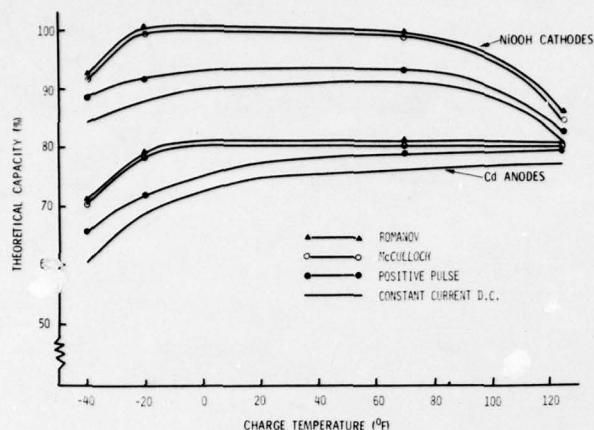
Figure 2. Capacity of NiOOH and Cd Electrodes vs. Charge Temperature.

McCulloch modes than with the d.c. mode in a temperature range of −40°F to about 100°F, (b) between 100°F and 125°F there was little difference in capacity as a function of mode, and (c) as compared to d.c., there was only a small improvement in capacity using the positive pulse mode.

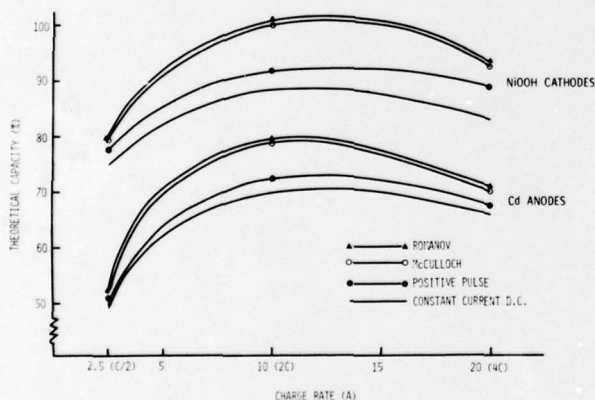Figure 3 shows the capacity of the NiOOH cathodes and

Figure 3. Capacity of NiOOH and Cd Electrodes vs. Charge Rate.

Cd anodes as percent of theoretical capacity versus charge rate. The charge temperature was −20°F. The data show that: (a) the maximum capacity for all four modes was at the 2C rate, and (b) at the lowest rate, (C/2), no significant difference in capacity was noted between the four modes.

It is interesting to note that, whereas the wave forms of the Romanov and McCulloch modes are radically different, there is little difference in their effect on the charge acceptance of the nickel-cadmium batteries. The positive peak on the Romanov mode is more than three times greater than that of the McCulloch mode, and the negative peak of the McCulloch mode is about 20 times greater than that of the Romanov mode. However, the energy of the negative pulse per cycle is practically the same for both modes; i.e., 2 to 2.5 milliwatt-seconds. If the energy of the negative pulse is the critical factor, in terms of increasing the charge acceptance of the

nickel and cadmium electrodes, then it should be possible to lower the positive and negative peaks by holding the energy of the negative pulse at a reasonably high value. Lowering the amplitudes of the pulses would simplify the charging circuitry by reducing its wattage. This, no doubt, would also lower the cost of the charger.

In order to determine the importance of the energy of the negative pulse, five-cell BB-616 Batteries were charged at various positive and negative pulse amplitudes and intervals. The temperature was held at the −20°F extreme while the charging rate was 2C and the frequency was 60 Hz. Figure 4
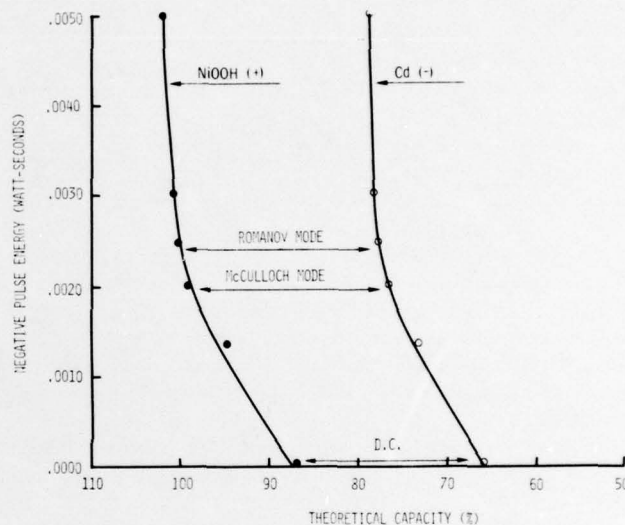

Figure 4. Capacity of the NiOOH and Cd Electrodes as a Function of Negative Pulse Energy.

shows the relationship between the energy of the negative pulse and the capacity of the nickel and cadmium electrodes. The capacities at the zero energy level represent the d.c. mode. From the figure it appears that a maximum capacity for both electrodes is attained at a minimum negative pulse energy of 2.5 milliwatt-seconds, thus confirming the original hypothesis of the importance of this factor.

To determine the effect charge frequency had on the capacity of nickel-cadmium batteries, the BB-616 Batteries were charged in a frequency range of 30 to 2000 Hz, holding the negative pulse energy in a range of 2 to 4 milliwatt-seconds. The charge temperature was −20°F and the charge rate was 2C. From the capacity versus frequency data of both electrodes, it became apparent that the capacity was independent of the frequencies tested.

An important finding of this investigation was that nickel-cadmium cells, which had lost capacity due to fadeout or crystal growth of cadmium and cadmium hydroxide, could be restored to their original capacity by one positive pulse charge cycle. Figure 5 shows discharge curves of the cadmium and nickel hydroxide electrodes of BB-616 cells that had been subjected to a fadeout regime and then reconditioned by a single positive pulse charge cycle. The half cell potentials were measured versus a mercury-mercuric oxide reference electrode. Originally, the capacity of the nickel cathode was
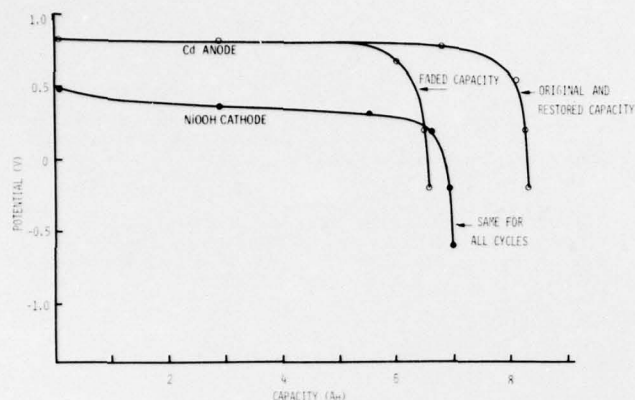
Figure 5. Capacity Lost by Fadeout and Restored by Pulse Charging.

6.9 Ah and that of the cadmium anode was 8.1 Ah. Fresh cells were subjected to a "fadeout cycle," which consisted of charging at 0.5 mA/cm^2 for 200 hours at 125°F and discharging at the same current density and temperature until the cadmium anodes were totally discharged. When the faded cells were subjected to three normal d.c. cycles, the nickel cathode capacity remained at 6.9 Ah, but the cadmium anode had dropped from 8.1 Ah to 6.5 Ah. In other words, the cells were cadmium limiting. A total of ten d.c. cycles could not restore the anode capacity lost during the "fadeout cycle." The faded cells were then given one positive pulse charge cycle at the C/2 rate. The frequency was 60 Hz, the pulse amplitude was 25 A for an interval of 1.8 ms., and the total input was 12 Ah. On the subsequent discharge the cadmium anodes delivered an average of 8.0 Ah, which was about the same as the original capacity.

Scanning electron micrographs were taken of the surface of the cadmium plates in the discharged state. Figure 6 shows

FRESH CONDITION   AFTER FADEOUT CYCLE
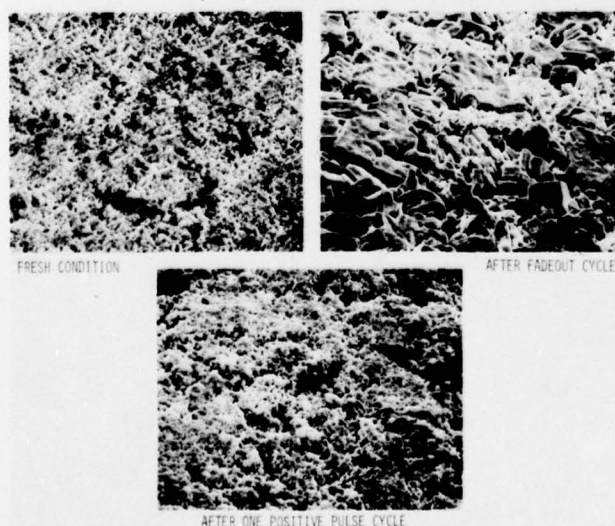
AFTER ONE POSITIVE PULSE CYCLE

Figure 6. Scanning Electron Micrographs of Cadmium Anode.

the micrographs of the cadmium anodes before and after

fadeout, and after one positive pulse cycle. The magnification is shown by the 10 micron marker in each photo. The view in the upper left-hand corner shows the anode in the fresh condition, where the hexagonal cadmium hydroxide crystals are about one micron in cross-section. The upper right-hand view shows the anode after the fadeout cycle. Here the crystals had grown to an enormous 50 to 100 microns in cross-section. Finally, the bottom view shows the anode condition after one pulse cycle. Here the cross-section of the crystals is reduced to about 3 to 5 microns. There is no doubt that these micrographs correlate very well with the capacity data shown in the preceding figure (Fig. 5).

After the pulse charge treatment, the cells were given several normal d.c. cycles. This cycling did not reduce the capacity of either the negative or positive electrode. This indicates that pulse charging should provide an excellent maintenance procedure for conditioning vented nickel-cadmium batteries that have lost capacity by "fadeout" and/or cell imbalance.

It should be pointed out that an optimum mode of reflex charging was carried out on an aged 11.0 Ah nickel-cadmium aircraft battery—type MS 18045-72. The capacity never went higher than 8.0 Ah by d.c. cycling, even with prolonged low rate overcharging and after changing the electrolyte. However, with two reflex charging cycles, the capacity increased to 13.0 Ah, which was 1.0 Ah less than that of a fresh battery. For this test the average charge rate was 20 amperes, the charge pulse amplitude was 50 amperes for 7.3 ms. and the discharge pulse amplitude was 5.0 amperes for 5 ms. The input was 20 ampere-hours. These data indicate the merits of using reflex charging as a maintenance charge procedure.

To determine whether there are any deleterious effects on the nickel-cadmium battery by continuous prolonged cycling on a reflex mode, a 5 cell E.P. BB-406 Battery was placed on an automatic regime at 60% depth of discharge at the C rates of charge and discharge, using the Romanov mode of charge. After every 50 cycles the battery was given three deep cycles to a 5.0 V cutoff to determine the true battery capacity. After 500 cycles the capacity remained constant at 100% of theoretical. This indicates that reflex charging will not impair the performance of the nickel-cadmium battery.

Beneficial effects of reflex charging were also observed with sealed cylindrical nickel-cadmium batteries, i.e., good charge acceptance, particularly at low temperatures, and the erasure of fadeout. Also, the heat generated by the sealed and vented batteries was the same for both the reflex and constant current d.c. modes. Charge control by a thermally regulated voltage cutoff was found to be practicable for vented nickel-cadmium batteries using both charging modes. However, for sealed batteries a novel pressure cutoff device was found to be just as effective and reliable as thermal cutoff. The study of charging methods for sealed nickel-cadmium batteries is continuing.

Conclusions

Reflex charging with an average charge rate of 2C, a frequency range of 30 to 2000 Hz, and a minimum negative pulse energy of 2.5 milliwatt-seconds increased the charge acceptance of vented and sealed nickel-cadmium batteries by 10

to 15 percent in the temperature range of −40°F to about 100°F.

Reflex charging and positive pulse charging provide an excellent means for restoring the capacity lost by vented and sealed nickel-cadmium batteries.
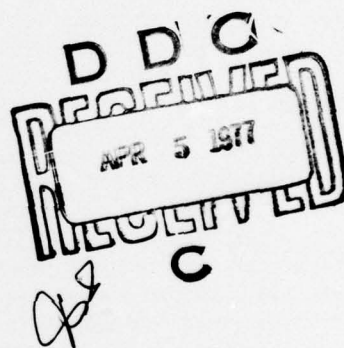
Life cycling of a vented nickel-cadmium battery using the reflex mode of charge showed that the battery maintained its capacity at about 100% of theoretical up to the 500 cycles tested.

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